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USE OF CFCs IN GROUNDWATER INVESTIGATIONS IN DUMAGUETE CITY AND INITIAL APPLICATION IN PHILIPPINE GEOTHERMAL FIELDS

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ABSTRACT

The use of Chlorofluorocarbon (CFC) tracing technique in Dumaguete City provided significant information on the groundwater flow dynamics of the Okoy and Banica watersheds. Water district wells 54 and 55, located east of the Palinpinon thermal area, are tapping groundwater with 11% to 80% recent recharge aging from 10 to 36 years old, respectively. Towards the southeast in the area of well 47, the groundwater becomes older than 60 years old. CFC and geochemical data confirmed that the wells within 54 are hydrologically connected to the River waters of both Okoy and Banica while the wells to the south are recharged from a different location on the upper slope of the Banica watershed.

Results of the initial application of the CFC technique in the Mt. Apo (MGPF) and Southern Negros Geothermal Production Field (SNGPF) suggest that there is about 7 to 42% recent groundwater recharge into the geothermal reservoirs having ages of 28 to 39 years old, respectively. The groundwater in the wells affected by injection fluid returns and cool water inflows were quantified using CFC data, which was correlated with existing geochemical, hydrological and stable isotope data. Based on initial results, 7% of the reservoir water at SNGPF is recent recharge while 19% comprise the recent recharge in the geothermal reservoir of MGPF. Further enhancement of data interpretation will provide more significant information that could be used as tool in reservoir management.

1.0 INTRODUCTION

The presence of Chlorofluorocarbons, or CFCs, in the atmosphere can be traced back to as early as the 1930's. These stable, synthetic, halogenated alkanes are believed to be entirely of anthropogenic origin, produced as safe alternatives to ammonia and sulphur dioxide in refrigeration and used as insulators, propellants in aerosols and as solvents. The most abundant compounds are CFC-12 (CCl_2F_2), CFC-11 (CCl_3F) and CFC-113 ($C_2Cl_3F_3$), make up more than 77% of the total CFCs. Other CFCs are present in the atmosphere and may prove to be useful tools for groundwater studies in the future (Plummer and Busenberg, 1992).

Rapid industrialization has increased the atmospheric level of CFCs. Based on production records and released data prior to 1977, and on the measured data at different stations since the mid-1970s, growth curves of atmospheric concentrations of CFCs from 1940 to the present have been reconstructed (Fig. 1) (Busenberg and Plummer, 1992; Cook and Solomon, 1995; Ekwurzel *et al.*, 1994; Szabo *et al.*, 1996; Wisegarver and Gammon, 1988).

The use of CFCs as tracing tools in groundwater studies started in the mid-1970s. The presence of CFCs in groundwater indicates recharge after

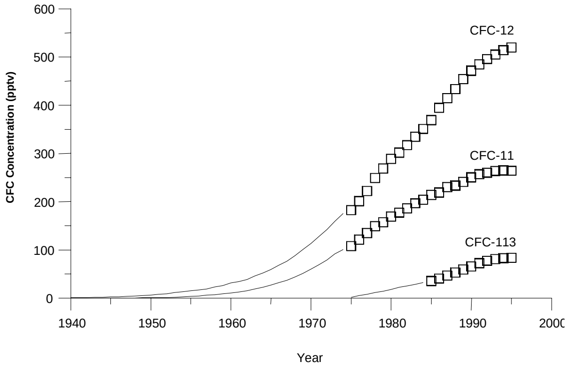

Figure 1. Global trends of atmospheric CFC concentrations. The lines represent industrial release data estimated from production records. The open squares represent measurements.

1950, or mixing of older waters with the post 1940 waters (Busenberg and Plummer, 1992; Cook and Solomon, 1995; Cook *et al.*, 1995; Cook *et al.*, 1996; Dunkle *et al.*, 1993; Ekwurzel *et al.*, 1994; Oster *et al.*, 1996; Szabo *et al.*, 1996).

As one can use atmospheric CFC source functions (Fig. 1) in groundwater investigations, there are also variations in the ratios of atmospheric CFC concentrations that can be used for groundwater investigations. Figure 2 shows the reconstruction of the ratios based on the data presented in Figure1.

This paper focuses on the use of CFCs in studies of mixed water systems. A case study on shallow groundwater in Dumaguete City by using CFCs is presented. Attempts at application of CFCs in the waters of the Southern Negros Geothermal Production Field (SNGPF) and Mt. Apo Geothermal Production Field (MGPF) were also made, aimed at possibly identifying and quantifying recent groundwater recharge into these geothermal systems.

2.0 CFC DATA INTERPRETATIONS AND APPLICATIONS

Ideally, all three different ages should agree in just one apparent age that indicates one single water mass without point-source CFC contamination. If all CFC's give different apparent ages, the oldest is CFC-12, CFC-11 is younger and CFC-113 the youngest. This indicates mixing of CFC-free old water and young water. If the calculated CFC-11 is low relative to CFC-12 and CFC-113, CFC-11 may be degraded and it is probable that the water is really old. In this case the age of the water is most likely closer to the CFC-12 and/or CFC-113. If CFC-12 is below the detection limit of 0.01 pmol/kg, no age can be assigned since the water is more than 60 years old. Traces of CFC-11 and CFC-113 could be present in such a case and would indicate contamination with air during sampling.

In cases where samples indicate a mixture of old and young waters, the dilution factors can be calculated by dividing the calculated CFC concentrations with the expected modern surface water concentrations. This will determine the percentage of the young and old waters and would provide additional information on the hydrologic flow conditions.

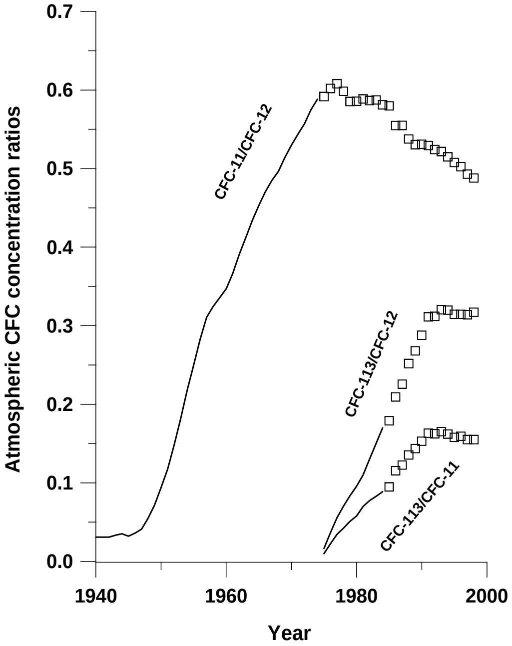

Figure 2. Time-dependent atmospheric concentration ratios of CFC-11/CFC-12, CFC-113/CFC-11, and CFC-113/CFC-12. Ratios are based on the data presented in Fig. 1.

The interpretations from the CFC data could be practically applied in groundwater aquifer management. The presence of modern water (CFC-containing water) in the well signifies that a certain percentage of water recharge comes from a lower elevation relative to the CFC-free waters. The existence of CFC also could indicate that the aquifer is under hydraulic stress due to either over-extraction or poor well design. The volume and quality of the groundwater being extracted would be at risk if the percentage of CFC-contaminated water increases. The potential for contamination from surface water would be greater if higher percentages of CFCs are present in the well. These are just some of the useful application of the tool.

Except for the case of a pure piston-type flow system, or of stationary waters entrapped in a geological formation, the measurements of CFC concentrations can give only the "apparent" groundwater age. Depending on the mixing model and the degree of mixing of 'older' and 'younger' components, the recharge years derived from CFC concentrations could potentially vary between 1940 and present time.

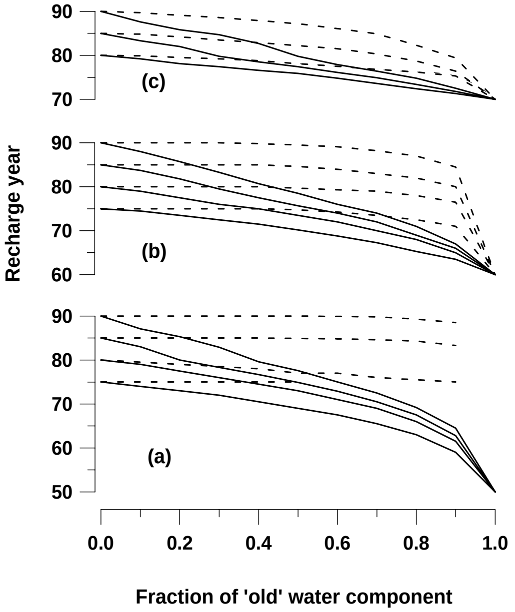

Figure 3. Effects of mixing of old component with young waters.

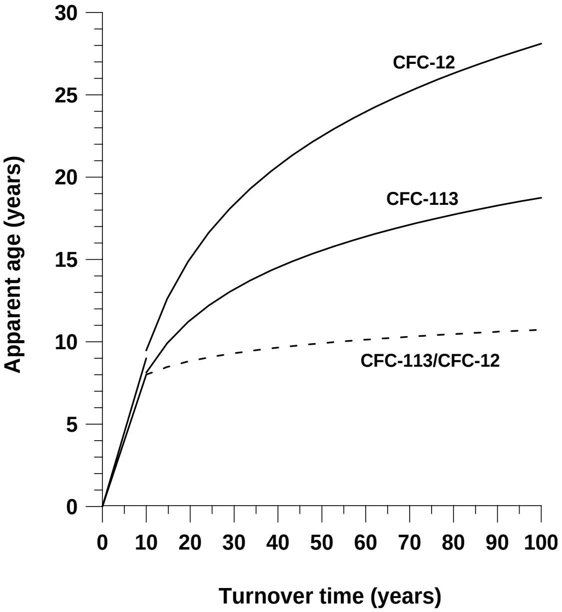

Figure 4. Apparent CFC ages in a completely mixed reservoir.

3.0 MIXING EFFECTS OF WATERS WITH DIFFERENT AGES

If a groundwater consists of components of different ages, as for example in a mixed flow system, care should be taken in interpreting CFC concentration data for age calculations.

In Figure 3, the effect of mixing of 1950, 1960 and 1970 waters with younger components are shown in (a), (b) and (c), respectively, for a simple “two-component mixing system”. Each point on the curve derived from the two CFC atmospheric concentration curves (according to data from Fig. 1) describes a distinct recharge year for a water sample. Data points on the curve most probably indicate piston-flow conditions (no mixing of water masses). Two sets of lines are shown, which both intersect the left y-axis and the curve at a certain recharge year. Any data point on such a line could be interpreted as a linear mixing between different water ages. This diagram provides not only information about mixing of waters but also information about the age of the young fraction and the mixing ratios. The diagram provides general information, if more than one sample is available, regarding the relationship of different samples. Also, it allows for easy identification of processes that modify CFC concentrations. For example, a point away from the area enclosed by the piston flow curve and the straight line with the greatest slope indicates the influence of other concentration modifying effects like CFC contamination or CFC degradation.

In this mixed system, depending on the degree of mixing, the recharge years derived from CFC concentrations could potentially vary between pre-1950 and present time. Unlike CFC concentrations, however, if a fraction of old water is added to a young water, unless the fraction of the old water component is very high, the CFC-113/CFC-12 ratio usually represents the age of the younger component, provided the old water is either free of CFCs or has relatively low CFC concentrations.

In Figure 4, the apparent CFC ages derived from CFC-12, CFC-113 and the ratio CFC-113/ CFC-12 are drawn against the turnover time of a “completely mixed reservoir system”. The apparent CFC ages increase as turnover time increases. However, discrepancies exist between the ages derived from CFC-12, CFC-113 and the ratio CFC-113/CFC-12. As the turnover time increases, the discrepancies become more significant.

In reservoir containing mixed waters of different ages, mixed flow systems can be identified by, 1) occurrence of CFC-113 while the CFC-12 age indicates that the water was recharged before 1975; 2) CFC-113/CFC-12 age is younger than both CFC-12 and CFC-113 age; 3) CFC-113 age is younger than CFC-12 age.

Two models can be use to calculate mixing ratios of older and younger contributions for a system which has been identified as a mixture of waters of different ages.

3.1 Two-Component Mixing Model

In this simplified model, the water is considered to be a mixture consisting of two components, namely: the younger CFC containing component and the older one which is CFC free. If fraction x of CFC free water is present with (1-x) of younger CFC containing water, the concentrations of CFCs in the mixture are:

$$[\mathrm{CFC-113}]_{\mathrm{mix}} = (1-x)[\mathrm{CFC-113}]_{y} \qquad (1)$$

$$[\mathrm{CFC-12}]_{\mathrm{mix}} = (1-x)[\mathrm{CFC-12}]_{y} \qquad (2)$$

where $[\mathrm{CFC-113}]_{\mathrm{mix}}$ and $[\mathrm{CFC-12}]_{\mathrm{mix}}$ are the CFC concentrations in the mixture, x is the fraction of CFC free component, $[\mathrm{CFC-113}]_{y}$ and $[\mathrm{CFC-12}]_{y}$ are the CFC concentrations in the younger component.

3.2 Completely Mixed Reservoir Model

The potential of fast contamination of a groundwater system has been one of the objectives of groundwater investigations. In such studies, unfortunately, the term ‘apparent age’ may mislead. This is because apparent ages are based on the simplifying assumption of piston flow, referring to the duration since recharge and isolation from the atmosphere. Consider for instance some samples of mixed waters with apparent ages ranging from 30 to 50 years. The user of the data who has no good understanding of the models may start to look for a relatively distant recharge area, and may think that there is no danger of a fast contamination. However, for such systems the fraction of waters with extremely young ages (theoretically equal to zero) may exist. For this reason, even in cases where responses of different models cannot be differentiated, the best practice may be to report not only the apparent ages but also the results obtained from other models. Moreover, Plummer and Bussenberg (2001) has demonstrated that it is difficult to identify modern water from a mixture if the old fraction is not ‘too’ old and contains some CFCs. In order to associate CFC data with pollution problems of a water system, the introduction of a new term ‘modern water equivalent’ into CFC data interpretation is suggested. This can be used to assess the groundwater vulnerability to ‘fast contamination’. To calculate ‘modern water equivalent’, one always assumes a water sample being a mixture of modern water with old ‘CFC-free’ water, the fraction of ‘modern water’ calculated under this assumption is then defined as ‘modern water equivalent’. This water could be actually a mixture containing modern water and other fractions which contain CFCs, or it could be a mixture without modern fraction, or even an unmixed sample. Obviously, due to possible existence of CFCs in the old fraction, or, due to the absence of the modern fraction, the calculated value may probably overestimate, but will never underestimate, the amount of the modern fraction, so that the potential danger of ‘fast contamination’ will not be overlooked.

4.0 APPLICATION IN DUMAGUETE WATER DISTRICT, SNGPF AND MGPF

4.1 Shallow Groundwater and Surface Water

The CFC technique has not been applied to a geothermal environment prior to this study. This is the first attempt to introduce it as a tool in the determination of recent recharge waters of meteoric origin or possible injection returns.

Water samples were collected from five (5) groundwater production wells of the Metro Dumaguete Water District (MDWD) and two (2) rivers (Okoy and Banica rivers) for CFC, stable isotope, tritium and chemistry analyses. Samples from six (6) geothermal production wells, the brine line 317 and a creek were collected for the same analyses at SNGPF. Among the geothermal wells of MGPF, two production wells, a sump, the Main Brine Line 1 (MBL1) and a river was likewise included in the study.

In the geothermal wells, samples were collected from both steam condensate and weber water but only the latter were successfully analyzed. Difficulty owing to instrument contamination from other volatile substances was experienced for the steam condensate samples from both SNGPF and MGPF. Only those samples from PN22, OK10D and the RI line 317 from SNGPF came out with reliable data. Similarly at MGPF,

Table 1. CFC and Isotope data at Dumaguete City, SNGPF and MGPF, Philippines.

Water Source	Determined CFC Conc.			Recharge Year			Apparent Ages			Concentration Ratio			del ^{18}O per mille	Remarks
	CFC-11	CFC-12	CFC-113	CFC-11	CFC-12	CFC-113	CFC-11	CFC-12	CFC-113	CFC-11	CFC-12	CFC-113		
	(pmol/kg)						Years			Calc. CFC/CFC modern air				
47	0.11	ND	0.01	1961	<1940	<1970	39	>60	>30	0.04	ND	0.04	-7.44	CFC-free water, indicating water is at least 50 years old (or >60 yrs old?). Presence of CFC-11 and CFC-113 indicate contamination during sampling (both are
46	0.29	0.09	0.01	1966	1960	< 1970	34	40	>30	0.12	0.06	0.05	-7.23	Mixed waters. CFC-free water is ~94-95% and recent water is ~5-6%. Relative age of old water is ~40 years old while younger water is at least 30 years old.
54	0.66	0.13	0.02	1972	1964	1976	28	36	24	0.33	0.11	0.11	-7.18	Mixed waters. CFC-free water is ~89% and recent component is ~11%. Old water is about 36 years old while younger water is about 24 years old. Relatively high CFC-11 concentration indicate possible contamination during sampling. Hence, high mixing ratio.
56	0.75	0.29	0.05	1972	1968	1979	28	32	21	0.31	0.20	0.23	-7.22	Mixed waters. CFC-free water is ~77-80% and recent component is ~20-23%. Older water is about 32 years old and younger water is 21 years old. The presence of relatively high percentage of recent component implies not-so-distant recharge area.
55	1.58	1.2	0.12	1981	1990	1986	19	10	14	0.67	0.87	0.58	-6.96	Either relatively young water with recharge years between 1986-1990, or mixed waters. CFC free water is ~13-42% and recent component is ~58-87%. Slightly enriched ^{18}O suggests inflow of isotopically depleted water (or evaporated surface water).
Banica River	2.09	2.42	0.15	1992		1988	8		12	0.89	1.75	0.72	-7.13	Slightly lower than the water which is in equilibrium with modern air, indicating discharge of groundwater into the river. Baseflow component of river discharge is about 28%.
Okoy River	2.24	1.26	0.18	1990	1994	1991	10	6	9	0.99	0.95	0.90	-7.15	Slightly lower than the water which is in equilibrium with modern air, indicating discharge of groundwater into the river. Baseflow component of river discharge is about 5-19%.
UPE - creek	2.91	1.27	0.32	1989	1988	< 1970	11	12	>30	0.97	0.74	1.16	-7.29	Why is this in equilibrium with modern air? My calculations show baseflow component of about 28%.
RI Rine 317	0.13	0.32	ND	1962	1970	< 1970	38	30	>30	0.06	0.23	ND	-2.84	Mixture of CFC-free water (77%) and recent water (23%) which is about 30 years old.. Among the recent water, younger water is about 6%.
MBL - MGPF	ND	0.31	ND	<1943	1968	< 1970	>57	32	>30	ND	0.19	ND		Mixture of CFC-free water (81%) and recent water (19%). Recent water is about 32
APO3D WBR	0.03	0.72	ND	1954	1976	< 1970	46	24	>30	0.01	0.42	ND		Mixture of CFC-free water (58%) and recent water (42%). Recent water is about 24
TM1D-WBR	0.02	0.56	0.01	1952	1972	1972	48	28	28	0.01	0.31	0.03		Mixture of FCF-free water (69%) and recent water (31%) with recharge year of 1972.
PN22-WBR	c	0.1	c	<1943	1961	< 1970	>57	39	>30	c	0.07	c	-2.69	Basically old water with only about 7% recent component which is about 39 years old.
OK10D WBR	c	0.1	c	<1943	1961	< 1970	>57	39	>30	c	0.07	c	-2.87	Basically old water with only about 7% recent component which is about 39 years old.

samples from APO3D, TM1D and the MBL1 gave some conclusive data.

Table 1 shows the CFC concentrations, the apparent ages of young waters and the summary of data interpretations. Among the 5 MDWD wells, well 47 was the only well which was CFC-free (CFC-12 is nil).

A trace of CFC-11 and CFC-113 was detected probably owing to contamination from air during sampling. This indicates that the water in the well is at least 50 years of age, which would also suggest that the recharge area of the aquifer tapped by the well is from a relatively higher elevation. Well 55 proved to have the youngest groundwater with more than 50% of the water having a relative age of only about 10 years. This could be attributed to the recharge coming from the nearby Okoy and Banica River systems.

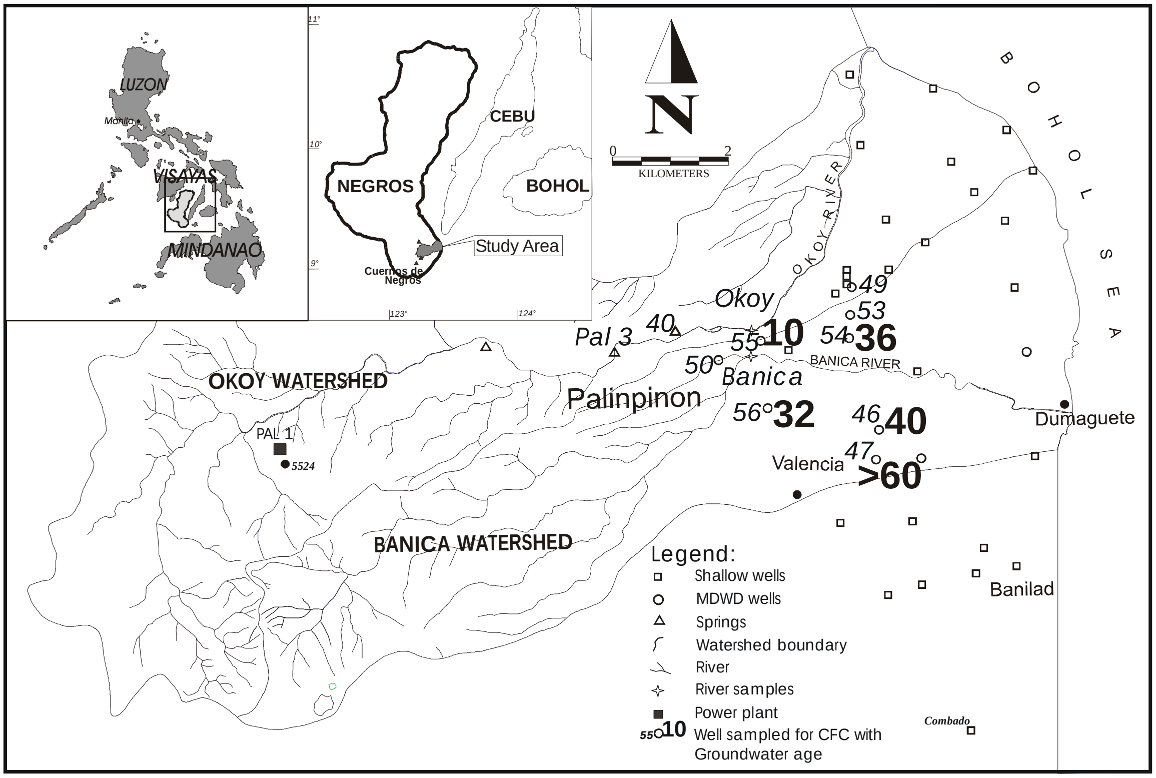

Figure 5. Apparent CFC ages from five wells at Dumaguete City, Philippines.

Well 46 contains mixed type of water, having about 95-96% CFC-free “old” water and 5-6% young water of about 40 years old. Younger groundwater based on the CFC-11 data is at least 30 years old. This could signify that about 6% of the water in the well is being recharged at relatively lower elevation than the older 94% water.

Well 54 is the well that has a sampling temperature of 32°C so the pressure correction factor for the 30°C was used in the calculations. The well has about 11% recent component with a recharge date of 1964, and contains 89% CFC-free groundwater. The relatively high CFC-11 concentration probably indicates air contamination during sampling. Hence, the high calculated mixing ratio of 5.08.

Well 56 was drilled in a reservoir with about 20-23% recent component and 77-80% old component (CFC-free) with relative ages of 21-32 years old and at least 50 years old, respectively. The presence of high percentage of recent water implies a not-so-distant recharge area.

Figure 5 shows the location of the groundwater wells and the apparent ages obtained. The age of the groundwater increases towards the southeast from about 10 years old in well 55 to more than 60 years old in well 47. Okoy and Banica Rivers appear to be infiltrating into the aquifer tapped by well 55 as shown by the relatively young water in the well. On the other hand, the aquifer within well 47 is being recharged by waters from higher elevation that takes more than 50 years of residence time to reach the area.

Both the Okoy and Banica rivers have CFC concentrations that are slightly lower modern air concentration, which indicate that river water receives groundwater as baseflow. This baseflow component for Banica River is 11-28% based on the concentration ratios of CFC-11 and CFC-113, respectively. For the Okoy River, the baseflow component could not be estimated since the CFC-11 concentration is higher than CFC-12 and CFC-113, indicating contamination with air during sampling.

4.2 Geothermal Wells

At SNGPF, production wells PN22D and OK10D were found to have CFC-12 concentration of 0.1 pmol/kg. This indicates that about 7% of the water in both wells are young water with recharge year of 1961 (39 years old) and 93% of the water is old.

Looking at the history of these wells, PN22D and OK10D are tapping acids fluids in the southeastern sector of Puhagan having low pH (≤ 4.0), high reservoir sulfate (>250 mg/kg) and high reservoir magnesium (<2.5 mg/kg). Anhydrite often deposited in these wells due to the inflow of acid-sulfate fluids (Seastres *et al.,* 1995). Sulfur isotope studies indicate that the originally acidic fluids at Palinpinon are produced from H_2S oxidation at shallow depths. The inflow of acid fluids was however suppressed by the breakthrough of injection fluids from well TC2RD in 1991, which proved beneficial for the Puhagan reservoir. Hence, these wells had been affected by injection fluid returns since. Moreover, based on extrapolation of pre-exploitation baseline isotopic data, the upwelling parent fluid is postulated to be a mixture of 80% meteoric water and 20% magmatic water (Gerardo *et al.*, 1993). Apparently this meteoric water was further quantified using CFC.

The CFC data obtained therefore suggests that out of the 80% meteoric waters in the geothermal reservoir, about 7% is 39 years old while the rest is pre-1969 waters. The most recent $\delta^{18}O$ value of -2.69 ‰ for well PN22D and -2.87 ‰ for well OK10D is relatively enriched compared to the parent fluid isotope composition of about -4.70 ‰, which indicates inflow of different fluids, possibly injection returns of enrichment due to boiling. Since the CFC data suggest that only about 7% of water is 39 years old, it is possible that the volume of injection fluids detected in the early 1990s have not affected the CFC concentration in the reservoir. Therefore, 7% recent recharge could possibly be meteoric in origin. One possible explanation why injection returns did not affect the CFC concentration is that the separated fluid was not exposed to the atmosphere. Exposure to the atmosphere would have changed the CFC value to near the threshold local atmospheric concentration.

In the RI line 317, CFC-12 concentration of 0.12 pmol/kg was detected, indicating that the geothermal waters being injected are a mixture of 77% CFC-free water and 33% 30-year old water.

At MGPF, five sampling stations were identified to establish the CFC concentrations in the area (Fig. 6). Kanlas River was included in the study to determine the threshold value in the field. Production well TM-1D, located at the upflow of the resource, was sampled both from steam condensate and webre water. Well APO-3D is also located at the upflow of the geothermal resource but was reported to be receiving injection returns. The Main Brine Line #1 (MBL1) was sampled to determine the CFC concentration of the injected water. The condensate water at pad RA sump was likewise determined.

Among the samples taken, only the webre water samples from MBL1, APO3D and TM1D successfully provided CFC concentrations. The same problem from volatile gas was encountered with the steam condensate samples.

Well APO3D has a CFC-12 concentration of 0.72 pmol/kg, which is equivalent to 42% of recent water component with relative age of 24 years old.

For well TM1D, CFC-12 and CFC-113 were concordant with one another with the young water having the same recharge year of 1972 (28 years old). TM1D is located in the upflow area of the geothermal field where reservoir temperature is about 280°C based on silica geothermometer with lower chloride content relative to projected parent fluid of ~ 6600 mg/kg (Sambrano, 1998). Dilution or mixing appears to be the main process affecting the fluids as it rises to shallower horizons of the reservoir. Stable isotope composition of waters tapped by TM1D shows relative depletion in $\delta^{18}O$ values compared to other wells in the upflow area. Hence, the dilution trend identified through chemistry could most probably be due to re-heated meteoric water recharge. The 31% recent meteoric water recharge has a relative age of about 28 years old based on CFC concentrations.

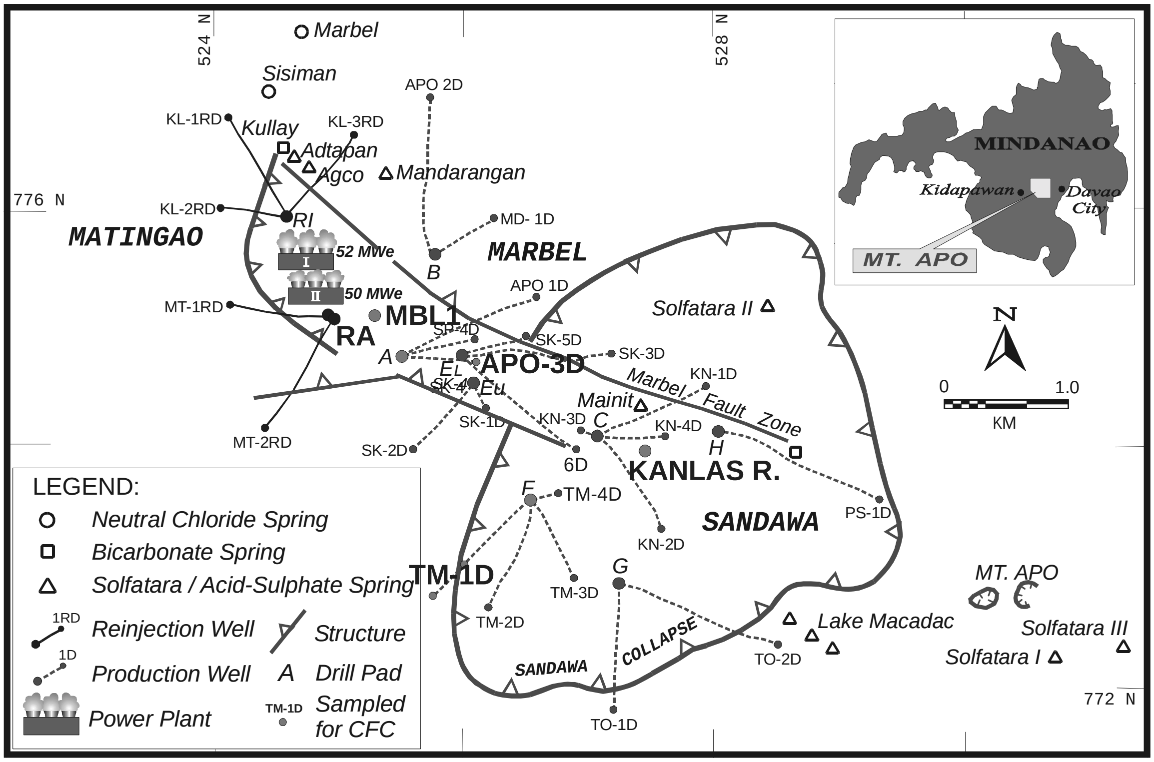

Figure 6. Location map of Mt. Apo geothermal production field and location of sampling stations for CFC.

Well APO-3D, on the other hand, has a higher recent water component of about 42% with relative age of 24 years old. This well is one of the wells that is possibly receiving cold meteoric recharge after a year of commercial exploitation (Esberto, et al., 1998). The 42% recent component in the well determined from CFC could be attributed to this recharge.

Along the MBL1, CFC data suggests 19% of relatively recent waters which is about 32 years old. Fluids along the MBL1 are mixtures of geothermal fluids from the production sector of Mindanao 1, and the percentage of recent component determined from CFC is the average recent component from the production wells. It could therefore be assumed that the average recent meteoric water recharge in the production wells supplying Mindanao-1 power plant is about 19%.

5.0 CONCLUSIONS

- The use of CFC technique in groundwater dating and tracer studies is a useful tool that could provide information on the relative ages of post 1950 waters. Determination on the mixing ratios of old and young waters quantifies how much water is introduced into the well. This method, however, should not be used as a stand-alone technique but rather be combined with other geochemical and isotopic data used in groundwater investigations.
- Groundwater at the lower Okoy and Banica watersheds increases in age towards the southeast. This suggests that groundwater recharge near well 55 is relatively closer and is influenced by river waters. The recharge of groundwater to the south then comes from a relatively higher elevation, signifying that the wells are producing waters recharged from different areas.
- The baseflow component of Banica River ranges from 11% to 28%, suggesting that the groundwater contributes to the total river discharge. The baseflow component of Okoy River could not be estimated due to possible contamination during sampling.
- CFC data from geothermal wells in SNGPF and MGPF provided additional information on the possible sources of fluids in the reservoir.

The age and proportions of the post 1940 waters were determined among wells identified to be receiving injection returns and cool acid inflow. Among wells in the upflow zone of the reservoir, CFC data suggests around 7% recent meteoric recharge for SNGPF and 19% for MGPF.

- Since this is the first application of CFC in geothermal environment, its use should be applied with caution and must be correlated with other available significant geological, geochemical, isotopic and hydrological data. Although the CFC data provided significant information on the proportions of waters in the geothermal reservoir, the data interpretation and correlation necessitates further understanding of the behavior of CFC at high temperature environment in order to fully assess its application as an additional tool in reservoir management.

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